

10.6: Types of Acids and Bases

Learning Objectives

- Given the formula of a **binary compound of hydrogen** with an element of $Z < 18$, predict whether its aqueous solution be acidic or basic, and write an appropriate equation.
- Do the same for an **oxygen- or hydroxy compound** of a similar element.
- Define an **oxyacid**, and explain why many of these are very **strong acids**.
- Write an equation describing the **amphoteric** nature of zinc or aluminum hydroxide.
- Define an **acid anhydride**, and write an equation describing its behavior.
- Explain how **metal cations** can give acidic solutions.
- Write equations showing why aqueous solutions of some **salts** are acidic, while others are alkaline.
- Write the formulas of an **organic acid** and an **organic base**, and write an equation showing why the latter gives an alkaline solution in water.

You will already have noticed that not every compound that contains hydrogen atoms is acidic; ammonia NH_3 , for example, gives an alkaline aqueous solution. Similarly, some compounds containing the group $-\text{OH}$ are basic, but others are acidic. An important part of understanding chemistry is being able to recognize what substances will exhibit acidic and basic properties in aqueous solution. Fortunately, most of the common acids and bases fall into a small number of fairly well-defined groups, so this is not particularly difficult.

Binary Hydrides

Strictly speaking, the term *hydride* refers to ionic compounds of hydrogen with the electropositive metals of [Groups 1-2](#); these contain the *hydride ion*, H^- , and are often referred to as "true" hydrides. However, the term is often used in its more general sense to refer to any binary compound MH_n in which M stands for any element. The hydride ion is such a strong base that it cannot exist in water, so salts such as sodium hydride react with water to yield hydrogen gas and an alkaline solution:



The more electronegative elements form covalent hydrides which generally react as acids, a well-known example being hydrogen chloride, a gas which dissolves readily in water to give the solution we know as hydrochloric acid



Most of the covalent hydrogen compounds are weak acids— in some cases, such as methane, CH_4 , so weak that their acidic properties are rarely evident. Many, such as H_2O and NH_3 , are amphiprotic. The latter compound, ammonia, is a weaker acid than H_2O , so it exhibits basic properties in water



but behaves as an acid in non-aqueous solvents such as liquid ammonia itself:



In general, the acidity of the non-metallic hydrides increases with the atomic number of the element to which it is connected. Thus as the element M moves from left to right across the periodic table or down within a group, the acids MH become stronger, as indicated by the acid dissociation constants shown at the right. Note that

- The formulas shown in red represent "strong" acids (that is, acids stronger than H_3O^+ .)
- Hydrofluoric acid is the only weak member of the hydrohalogen acids.
- Acids weaker than water do not behave as acids in aqueous solution. Thus for most practical purposes, methane and ammonia are not commonly regarded as acids. H_2O itself is treated as an acid only in the narrow context of aqueous solution chemistry.

CH ₄ 10 ⁻⁴⁶	NH ₃ 10 ⁻³⁵	H ₂ O 10 ⁻¹⁶	HF 10 ⁻³
	PH ₃ 10 ⁻²⁷	H ₂ S 10 ⁻⁷	HCl 10 ⁷
		H ₂ Te 10 ⁻³	HBr 10 ⁹
			HI 10 ¹⁰

Attempts to explain these trends in terms of a single parameter such as the electronegativity of M tend not to be very useful. The reason is that acid strengths depend on a number of factors such as the strength of the M-H bond and the energy released when the resultant ions become hydrated in solution. This last factor plays a major role in making HF something of an anomaly amongst the strong acids of Group 17.



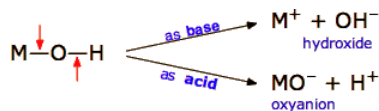
Ammonia is such a weak acid that its conjugate base, amide ion NH₂⁻, cannot exist in water. In aqueous solution, NH₃ acts as a weak base, accepting a proton from water and leaving a OH⁻ ion. An aqueous solution of NH₃ is sometimes called “ammonium hydroxide”. This misnomer reflects the pre-Brønsted view that all bases contain –OH units that yield hydroxide ions on dissociation according to the Arrhenius scheme



A solution of ammonia in water is more correctly referred to as "aqueous ammonia" and represented by the formula NH₃(aq). There is no physical evidence for the existence of NH₄OH, but the name seems to remain forever etched on reagent bottles in chemical laboratories and in the vocabularies of chemists.

Hydroxy Compounds

Compounds containing the *hydroxyl group* –OH constitute the largest category of acids, especially if the organic acids (discussed separately farther on) are included. M–OH compounds also include many of the most common bases.



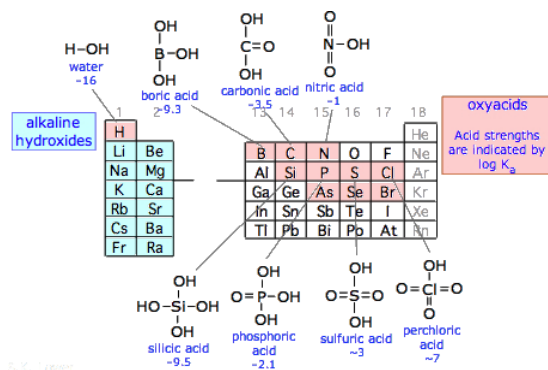
Whether a compound of the general type M–O–H will act as an acid or a base depends is influenced by the relative tendencies of the M–O and the O–H bonds to break apart in water. If the M–O bond cleaves more readily, then the –OH part will tend to retain its individuality and with its negative charge will become a hydroxide ion. If the O–H bond breaks, the MO-part of the molecule will remain intact as an *oxyanion* MO⁻ and release of the proton will cause the MOH compound to act as an acid.

This is not solely a matter of the relative strengths of the two bonds; the energy change that occurs when the resulting ions interact with water molecules is also an important factor.

In general, if M is a metallic element, the metal hydroxide compound MOH will be basic. The case of the highly electropositive elements of Groups 1 and 2 is somewhat special in that their solid MOH compounds exist as interpenetrating lattices of metal cations and OH⁻ ions, so those that can dissolve readily in water form strongly alkaline solutions; KOH and NaOH are well known examples of strong bases. From the Brønsted standpoint, these different “bases” are really just different sources for the single strong base OH⁻. As one moves into Group 2 of the periodic table the M–OH compounds become less soluble; thus a saturated solution of Ca(OH)₂ (commonly known as *limewater*) is only weakly alkaline. Hydroxides of the metallic elements of the p-block

and of the transition metals are so insoluble that their solutions are not alkaline at all. Nevertheless these solids dissolve readily in acidic solutions to yield a salt plus water, so they are formally bases.

The acidic character of hydroxy compounds of the nonmetals, known collectively as *oxyacids*, is attributed to the displacement of negative charge from the hydroxylic oxygen atom by the electronegative central atom. The net effect is to make the oxygen slightly more positive, thus easing the departure of the hydrogen as H^+ . The presence of other electron-attracting groups on the central atom has a marked effect on the strength of an oxyacid. Of special importance is the doubly-bonded oxygen atom. With the exception of the halogen halides, all of the common strong acids contain one or more of these oxygens, as in sulfuric acid $\text{SO}_2(\text{OH})$, nitric acid $\text{NO}_2(\text{OH})$ and phosphoric acid $\text{PO}(\text{OH})_3$. In general the strengths of these acids depends more on the number of oxygens than on any other factor, so periodic trends are not so important.



Most of the halogen elements form more than one oxyacid. Fluorine is an exception; being more electronegative than oxygen, no oxyacids of this element are known. Chlorine is the only halogen for which all four oxyacids are known, and the K_a values for this series show how powerfully the Cl-O oxygen atoms affect the acid strength.

Oxygen compounds

Binary oxides that contain no hydrogen atoms can exhibit acid-base behavior when they react with water. The division between acidic and basic oxygen oxides largely parallels that between the hydroxy compounds. The oxygen compounds of the highly electropositive metals of Groups 1-2 actually contain the *oxide ion* O^{2-} . This ion is another case of a proton acceptor that is stronger than OH^- , and thus cannot exist in aqueous solution. Ionic oxides therefore tend to give strongly alkaline solutions:



In some cases, such as that of MgO , the solid is so insoluble that little change in pH is noticed when it is placed in water. CaO , however, which is known as *quicklime*, is sufficiently soluble to form a strongly alkaline solution with the evolution of considerable heat; the result is the slightly-soluble *slaked lime*, $\text{Ca}(\text{OH})_2$. Oxygen compounds of the transition metals are generally insoluble solids having rather complex extended structures. Although some will dissolve in acids, they display no acidic properties in water.

Amphoteric oxides and hydroxides

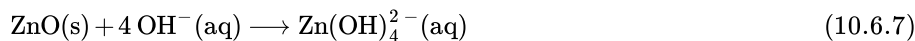
The oxides and hydroxides of the metals of Group 3 and higher tend to be only weakly basic, and most display an amphoteric nature. Most of these compounds are so slightly soluble in water that their acidic or basic character is only obvious in their reactions with strong acids or bases. In general, these compounds tend to be more basic than acidic; thus the oxides and hydroxides of aluminum, iron, and zinc all dissolve in mildly acidic solutions, whereas they require treatment with concentrated hydroxide ion solutions to react as acids.

$\text{Al}(\text{OH})_3 + 3 \text{H}^+ \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{H}_2\text{O}$	$\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^- \rightarrow \text{Al}(\text{OH})_3^- (\text{aq})$
$\text{Zn}(\text{OH})_2 + 3 \text{H}^+ \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	$\text{Zn}(\text{OH})_2(\text{s}) + 2 \text{OH}^- \rightarrow \text{Zn}(\text{OH})_3^{4-}(\text{aq})$
$\text{FeO}(\text{OH}) + 3 \text{H}^+ \rightarrow \text{Fe}^{3+}(\text{aq}) + 3\text{H}_2\text{O}$	$\text{Fe}_2\text{O}_3(\text{s}) + 3 \text{OH}^- \rightarrow 2 \text{FeO}_2^-(\text{aq}) + 3 \text{H}_2\text{O}$

The product ions in the second column are known as aluminate, zincate, and ferrate. Other products, in which only some of the -OH groups of the parent hydroxides are deprotonated, are also formed, so there are actually whole series of these oxyanions for

most metals.

An *amphoteric* substance is one that can act as either an acid or a base. An *amphiprotic* substance can act as either a proton donor or a proton acceptor. So all amphiprotic compounds are also amphoteric. An example of an amphoteric compound that is not amphiprotic is ZnO, which can act as an acid even though it has no protons to donate:



As a base, it "accepts" protons but does not retain them:



The same remarks can be made about the other compounds shown in the table above. For most practical purposes, the distinction between amphiprotic and amphoteric is not worth worrying about.

Acid anhydrides

The binary oxygen compounds of the non-metallic elements tend to produce acidic solutions when they are added to water. Such compounds are sometimes referred to as *acid anhydrides* ("acids without water").



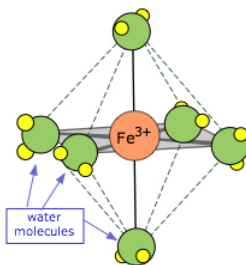
In some cases, the reaction involves more than simply incorporating the elements of water. Thus nitrogen dioxide, used in the commercial preparation of nitric acid, is not an anhydride in the strict sense:



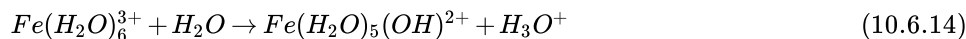
Metal cations as acids

When sodium chloride is dissolved in pure water, the pH remains unchanged because neither ion reacts with water. However, a solution of magnesium chloride will be faintly acidic, and a solution of iron(III) chloride FeCl_3 will be distinctly so. How can this be? Since none of these cations contains hydrogen, we can only conclude that the protons come from the water.

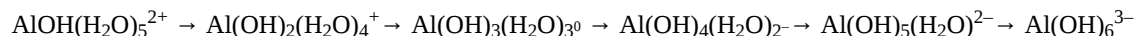
The water molecules in question are those that find themselves close to any cation in aqueous solution; the positive field of the metal ion interacts with the polar H_2O molecule through ion-dipole attraction, and at the same time increases the acidity of these loosely-bound waters by making facilitating the departure H^{+} ion. In general, the smaller and more highly charged the cation, the more acidic will it be; the acidity of the alkali metals and of ions like $\text{Ag}^{+}(\text{aq})$ is negligible, but for more highly-charged ions such as Mg^{2+} , Pb^{2+} and Al^{3+} , the effect is quite noticeable.



Most of the transition-metal cations form organized **coordination complexes** in which four or six H_2O molecules are chemically bound to the metal ion where they are well within the influence of the coulombic field of the cation, and thus subject to losing a proton. Thus an aqueous solution of " Fe^{3+} " is really a solution of the ion *hexaaquo iron III*, whose first stage of "dissociation" can be represented as



As a consequence of this reaction, a solution of FeCl_3 turns out to be a stronger acid than an equimolar solution of acetic acid. A solution of FeCl_2 , however, will be a much weaker acid; the +2 charge is considerably less effective in easing the loss of the proton. It should be possible for a hydrated cation to lose more than one proton. For example, an $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion should form, successively, the following species:



However, removal of protons becomes progressively more difficult as the charge decreases from a high positive value to a negative one; the last three species have not been detected in solution. In dilute solutions of aluminum chloride the principal species are actually $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (commonly represented simply as Al^{3+}) and $\text{AlOH}(\text{H}_2\text{O})_5^{2+}$ (" AlOH^{2+} ").

Salts

When salts dissolve in water, they yield solutions of anions and cations, so their effects on the pH of the solution will depend on the properties of the particular pair of ions. For a salt such as sodium chloride, the solution will remain neutral because sodium ions have no acidic properties and chloride ions, being conjugate to the strong acid HCl have negligible proton-accepting tendencies. Ions of this kind are often referred to as "strong" ions (that is, derived from a strong acid and a strong base—HCl and NaOH in the case of NaCl.) The possible outcomes for the other three possibilities are shown below.

salt derived from	example	pH	reaction
weak acid + strong base	NaF	>7	$\text{F}^- + \text{H}_2\text{O} \rightarrow \text{HF} + \text{OH}^-$
strong acid + weak base	NH_4Cl	<7	$\text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{H}_3\text{O}^+$
weak acid + weak base	NH_4F	?	depends on competition between above two reactions; need to do calculation

The reactions that cause salt solutions to have non-neutral pH values are sometimes still referred to by the older term *hydrolysis* ("water splitting")—a reminder of times before the concept of proton transfer acid-base reactions had developed.

Organic Acids and Bases

The *carboxyl group* $-\text{CO}(\text{OH})$ is the characteristic functional group of the organic acids. The acidity of the carboxylic hydrogen atom is due almost entirely to electron-withdrawal by the non-hydroxylic oxygen atom; if it were not present, we would have an alcohol $-\text{COH}$ whose acidity is smaller even than that of H_2O . This partial electron withdrawal from one atom can affect not only a neighboring atom, but that atom's neighbor as well. Thus the strength of a carboxylic acid will be affected by the bonding environment of the carbon atom to which it is connected. This propagation of partial electron withdrawal through several adjacent atoms is known as the *inductive effect* and is extremely important in organic chemistry.

A very good example of the inductive effect produced by chlorine (another highly electronegative atom) is seen by comparing the strengths of acetic acid and of the successively more highly substituted chloroacetic acids:

$\text{CH}_3\text{--COOH}$ acetic acid 1.8×10^{-5}	$\text{ClCH}_2\text{--COOH}$ monochloroacetic acid 0.0014	$\text{Cl}_2\text{CH--COOH}$ dichloroacetic acid 0.055	$\text{Cl}_3\text{C--COOH}$ trichloroacetic acid 0.63
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Phenols

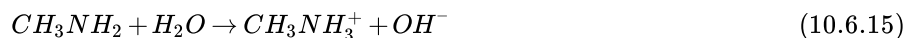
The acidic character of the carboxyl group is really a consequence of the enhanced acidity of the $-\text{OH}$ group as influenced by the second oxygen atom that makes up the $-\text{COOH}$ group. The benzene ring has a similar although weaker electron-withdrawing effect, so hydroxyl groups that are attached to benzene rings also act as acids. The most well known example of such an acid is phenol, $\text{C}_6\text{H}_5\text{OH}$, also known as *carbolic acid*. Compared to carboxylic acids, phenolic acids are quite very weak, as indicated by the acid dissociation constants listed below:

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$\text{CH}_3\text{-COOH}$ acetic acid 1.8×10^{-5}	$\text{C}_6\text{H}_5\text{-OH}$ phenol 1.1×10^{-10}	$\text{C}_6\text{H}_5\text{-COOH}$ benzoic acid 6.3×10^{-5}
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Amines and organic bases

We have already discussed organic acids, so perhaps a word about organic bases would be in order. The -OH group, when bonded to carbon, is acidic rather than basic, so alcohols are not the analogs of the inorganic hydroxy compounds. The amines, consisting of the -NH_2 group bonded to a carbon atom, are the most common class of organic bases. Amines give weakly alkaline solutions in water:



Amines are end products of the bacterial degradation of nitrogenous organic substances such as proteins. They tend to have rather unpleasant “rotten fish” odors. This is no coincidence, since seafood contains especially large amounts of nitrogen-containing compounds which begin to break down very quickly. *Methylamine* CH_3NH_2 , being a gas at room temperature, is especially apt to make itself known to us. Addition of lemon juice or some other acidic substance to fish will convert the methylamine to the methylaminium ion CH_3NH_3^+ . Because ions are not volatile they have no odor.

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